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**Method of removing soot from lubricating oils.**

Soot can be effectively removed from a lubricating oil used in a non-gasoline fueled internal combustion engine by contacting the oil with a heterogenous strong base. This results in improved engine cleanliness and reduced engine wear.

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## METHOD OF REMOVING SOOT FROM LUBRICATING OILS

This invention concerns removing soot from a lubricating oil for non-gasoline fueled internal combustion engines.

During combustion of fuel in a non-gasoline fueled internal combustion engine (e.g. a diesel engine), fuel is injected into the combustion chamber in the form of small droplets, which undergo a complex combustion process that includes pyrolysis (i.e., thermal decomposition). If the combustion is complete, the fuel droplet is converted to carbon dioxide and water. However, if the combustion is incomplete, the remainder of the fuel droplet often forms a soot particle because some incompletely combusted fuel droplets will reach the relatively cool cylinder wall where combustion is sharply reduced and soot particles are formed. When the piston travels to its uppermost position, the soot particle is covered by a film of lubricating oil. The oil laden soot is then scraped into the engine lubricating oil reservoir by the piston rings as the piston travels down the cylinder.

For many years, dispersants have been used in lubricating oils to suspend soot. This in turn reduces the soot's detrimental effect on engine wear. However, at some point, an oil's capacity to protect an engine becomes limited, even with the most potent dispersant. In addition, soot particles are usually so small and finely dispersed that currently available filters are generally not satisfactory for soot removal. Although centrifugal filters can remove larger soot particles, they effect only a partial removal of soot from the lubricating oil.

Therefore, it would be desirable to have available a simple, yet convenient method for removing soot from a lubricating oil and thereby avoid the deleterious effects of leaving the soot suspended in the oil.

This invention provides a method for removing soot from a lubricating oil by contacting the soot with a heterogenous strong base. More specifically, soot can be effectively removed from a lubricating oil used in a non-gasoline fueled internal combustion engine by contacting the soot with a heterogenous strong base. By "heterogenous" is meant that the strong base is in a separate phase (or substantially in a separate phase) from the lubricating oil; i.e. the strong base is insoluble or substantially insoluble in the oil. When the soot in the oil contacts the strong base, the soot (which has an acidic surface) reacts with the strong base and becomes immobilized on it as a deposit. Thus, soot is removed from the oil. The strong base should be immobilized in some manner (e.g. within a container or housing) when contacting the oil to avoid passing into or along with the oil.

By "strong base" is meant essentially any base that will cause the soot (which has an acidic surface) in the oil to become immobilized as deposits on the base or on a substrate if one is used. Examples of suitable strong bases include, but are not limited to, barium oxide ( $\text{BaO}$ ), calcium hydroxide ( $\text{Ca(OH)}_2$ ), magnesium carbonate ( $\text{MgCO}_3$ ), magnesium hydroxide ( $\text{Mg(OH)}_2$ ), magnesium oxide ( $\text{MgO}$ ), sodium aluminate ( $\text{NaAlO}_2$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium hydroxide ( $\text{NaOH}$ ), zinc oxide ( $\text{ZnO}$ ), or their mixtures. Magnesium oxide, sodium hydroxide, zinc oxide, or mixtures thereof are preferred. Magnesium oxide, sodium hydroxide, or mixtures thereof are particularly preferred, with magnesium oxide being most preferred.

The precise amount of strong base required can vary broadly depending upon the amount of soot in the oil. However, although only an amount effective (or sufficient) to reduce the soot content of the lubricating oil need be used, the amount will typically range from about 0.1 to about 20 wt.%, preferably from about 0.5 to about 10 wt.%, and most preferably from about 0.5 to about 5 wt.%, based on weight of the lubricating oil.

If desired, the strong base can be incorporated (e.g. impregnated) on or with a substrate. The substrate may be located within the lubrication system of an internal combustion engine (e.g. on the engine block or near the sump) or outside of the engine's lubrication system. Preferably, the substrate will be part of the filter system for filtering oil, although it could be separate therefrom. The strong base may be chemically bound to the substrate or physically incorporated into the substrate. Examples of suitable substrates include, but are not limited to, alumina, activated clay, cellulose, cement binder, silicaalumina, polymer matrices, and activated carbon. High surface substrates such as alumina, cement binder, polymer matrices, and activated carbon are preferred. The substrate can be formed into various shapes such as pellets or spheres. In addition, the substrate may (but need not) be inert.

The strong base may be incorporated on or with the substrate by methods known to those skilled in the art. For example, if the substrate were alumina spheres, the strong base can be deposited by using the following technique. A highly porous alumina is selected. The porosity of the alumina is determined by weighing dried alumina and then immersing it in water. The alumina is removed from the water and the surface water removed by blowing with dry air. The alumina is then reweighed and compared to the dry

alumina weight. The difference in weight is expressed as grams of water per dram of dry alumina. A saturated solution of calcium hydroxide in water is prepared. This solution is then added to the dry alumina in an amount equal to the difference between the weight of wet and dry alumina. The water is removed from the alumina with heat leaving  $\text{Ca}(\text{OH})_2$  deposited on the alumina as the product. This preparation can be carried out at ambient conditions, except the water removal step is performed above  $100^\circ\text{C}$ .

Once the soot has been removed from the oil, the deposits thus formed will be immobilized as heterogenous deposits with the strong base or with the strong base on a substrate if one is used. Thus, soot which would normally remain dispersed in the oil is removed therefrom as deposits.

Soot may be present in essentially any lubricating oil used in the lubrication system of essentially any non-gasoline fueled internal combustion engine. Thus, as used herein, "internal combustion engine", refers to essentially any internal combustion engine except those that are gasoline fueled. This includes non-gasoline fueled automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad engines, gas-fired engines, alcohol (e.g., methanol) powered engines, stationary powered engines, turbines, and the like. However, soot is primarily a problem in compression ignition engines such as diesel engines, especially modern design diesel engines with high fuel injection pressure. The trend in diesel engine design of increasing the fuel injection pressure to produce smaller fuel droplet size will likely exacerbate the problem because, although smaller fuel droplet size produces less particulate emissions, the formation of soot in lubricating oil is often increased.

In addition to soot, the lubricating oil will normally comprise a major amount of lubricating oil basestock (or lubricating base oil), and a minor amount of one or more additives. The lubricating oil basestock can be derived from natural lubricating oils, synthetic lubricating oils, or mixtures thereof. In general, the lubricating oil basestock will have a viscosity in the range of about 5 to about 10,000 cSt at  $40^\circ\text{C}$ , although typical applications will require an oil having a viscosity ranging from about 10 to about 1,000 cSt at  $40^\circ\text{C}$ .

Natural lubricating oils include animal oils, vegetable oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale.

Synthetic oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc., and mixtures thereof); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzene, etc.); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.); alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogs, and homologs thereof; and the like.

Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof wherein the terminal hydroxyl groups have been modified by esterification, etherification, etc. This class of synthetic oils is exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide; the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500); and mono- and poly-carboxylic esters thereof (e.g., the acetic acid esters, mixed  $\text{C}_3$ - $\text{C}_8$  fatty acid esters, and  $\text{C}_{13}$  oxo acid diester of tetraethylene glycol).

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid, and the like.

Esters useful as synthetic oils also include those made from  $\text{C}_5$  to  $\text{C}_{12}$  monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol, and the like. Synthetic hydrocarbon oils are also obtained from hydrogenated oligomers of normal olefins.

Silicon-based oils (such as the polyakyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. These oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxo)-disiloxane, poly(methyl)-siloxanes and poly(methylphenyl) siloxanes, and the like. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid), polymeric

tetrahydrofurans, polyalphaolefins, and the like.

The lubricating oil may be derived from unrefined, refined, rerefined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained  
 5 directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewax-  
 10 ing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Rerefined oils are obtained by treating refined oils in processes similar to those used to obtain the refined oils. These rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

The lubricating base oil may contain one or more additives to form a fully formulated lubricating oil. Such lubricating oil additives include antiwear agents, antioxidants, corrosion inhibitors, detergents, disper-  
 15 sants, pour point depressants, extreme pressure additives, viscosity index improvers, friction modifiers, and the like. These additives are typically disclosed, for example, in "Lubricant Additives" by C.V. Smalheer and R. Kennedy Smith, 1967, pp. 1-11 and in U.S. Patent 4,105,571, the disclosures of which are incorporated herein by reference. Normally, there is from about 1 to about 20 wt.% of these additives in a fully formulated lubricating oil. However, the precise additives used (and their relative amounts) will depend upon  
 20 the particular application of the oil.

This invention can also be combined with the removal of carcinogenic components from a lubricating oil, as is disclosed in European Patent Application 883000930.3 (published July 20, 1988 having Publication No. 0 275 148), the disclosure of which is incorporated herein by reference. For example, polynuclear aromatic hydrocarbons (especially PNA's with at least three aromatic rings) that are usually present in used  
 25 lubricating oil can be removed (e.g., reduced by from about 40 to about 90% or more) by passing the oil through a sorbent. The sorbent may be immobilized with the substrate described above or immobilized separate therefrom. The sorbent may also be the substrate upon which the strong base is immobilized. Preferably, the substrate and sorbent will be located within the lubrication system of an internal combustion engine through which the oil must circulate after being used to lubricate the engine. Most preferably, the  
 30 substrate and sorbent will be part of the engine filter system for filtering oil. If the latter, the sorbent can be conveniently located on the engine block or near the sump, preferably downstream of the oil as it circulates through the engine (i.e., after the oil has been heated). Most preferably, the sorbent is downstream of the substrate.

Suitable sorbents include activated carbon, attapulgus clay, silica gel, molecular sieves, dolomite clay,  
 35 alumina, zeolite, or mixtures thereof. Activated carbon is preferred because (1) it is at least partially selective to the removal of polynuclear aromatics containing more than 3 aromatic rings, (2) the PNA's removed are tightly bound to the carbon and will not be leached-out to become free PNA's after disposal, (3) the PNA's removed will not be redissolved in the used lubricating oil, and (4) heavy metals such as lead and chromium may be removed as well. Although most activated carbons will remove PNA's to some  
 40 extent, wood and peat based carbons are significantly more effective in removing four and higher ring aromatics than coal or coconut based carbons.

The amount of sorbent required will depend upon the PNA concentration in the lubricating oil. Typically, for five quarts of oil, about 20 to about 150 grams of activated carbon can reduce the PNA content of used lubricating oil by up to 90%. Used lubricating oils usually contain from about 10 to about 10,000 ppm of  
 45 PNA's.

It may be necessary to provide a container to hold the sorbent, such as a circular mass of sorbent supported on wire gauze. Alternatively, an oil filter could comprise the sorbent capable of combining with polynuclear aromatic hydrocarbons held in pockets of filter paper. These features would also be applicable to the substrate described above.

Any of the foregoing embodiments of this invention can also be combined with a sorbent (such as those described above) that is mixed, coated, or impregnated with additives normally present in lubricating oils, particularly engine lubricating oils (see European Patent Application 88300090.3). In this embodiment, additives (such as the lubricating oil additives described above) are slowly released into the lubricating oil to replenish the additives as they are depleted during use of the oil. The ease with which the additives are  
 50 released into the oil depends upon the nature of the additive and the sorbent. Preferably, however, the additives will be totally released within 150 hours of engine operation. In addition, the sorbent may contain from about 50 to about 100 wt.% of the additive (based on the weight of activated carbon), which generally corresponds to 0.5 to 1.0 wt.% of the additive in the lubricating oil.

Thus, this invention can be combined with removing PNA's from a lubricating oil, enhancing the performance of a lubricating oil by releasing conventional additives into the oil, or to both. In these embodiments, the substrate (if one is used) and sorbent may comprise the same material.

Although this invention has heretofore been described with specific reference to lubricating oils used in non-gasoline fueled internal combustion engines, it can also be suitably applied to essentially any oil (e.g. industrial lubricating oils) that contains soot.

This invention may be further understood by reference to the following examples which are not intended to restrict the scope of the appended claims. In these examples, the amount of soot in an oil sample was determined by thermal gravimetric analysis (TGA). TGA is an analytical technique in which an oil sample suspended on an arm of a thermobalance is heated and held within the constant temperature zone of a furnace through which a controlled atmosphere is passed. The loss or gain in sample weight is measured as a function of a temperature program applied to the furnace. The composition of the gas flowing through the furnace can be changed during the test run. A TGA procedure has been described by McGeehan and Fontana (Effect of Soot on Piston Deposits and Crankcase Oils -- Infrared Spectrometric Technique for Analyzing Soot, SAE paper, 801368, 1981). Another TGA method is described in ASTM E1131, Standard Test Method for Compositional Analysis by Thermogravimetry.

However, the particular TGA procedure employed in the examples below uses temperature and gas profiles that differ from those in the above two references as follows: the temperature was raised from 25° C (room temperature) to 600° C at a rate of 20° C/minute in an N<sub>2</sub> atmosphere; at 600° C the atmosphere was switched to air and the temperature held for 5 minutes; and the temperature was then raised to 680° C at a rate of 20° C/minute. All the weight loss after air replaced N<sub>2</sub> is considered as fixed carbon. As used herein, soot refers to the amount of pyrolyzable hydrocarbon and fixed carbon.

#### Example 1 - Soot Removal Using NaOH on Carbon

Used oil from a Mack T7 engine test was used to demonstrate the ability of a strong base to reduce the viscosity of the used oil by removing soot from the oil. The viscosity of the used oil before treatment with strong base was 26.6 centistokes at 100° C and 257.5 centistokes at 40° C. In this example, 2,000 grams of used oil was circulated at a rate of 2,000 ml/min through a filter containing 170 grams of NaOH on an activated carbon substrate. After 8 hours the viscosity of the oil was 17.7 centistokes at 100° C and 145.6 centistokes at 40° C. Using the modified TGA procedure described above, the amount of soot in the oil before and after contact with the NaOH on carbon was measured to be 20.6% and 10.7%, respectively, which corresponds to a 48.1% reduction in soot. The results obtained from this example are summarized in Table 1 below.

#### Example 2 - Soot Removal Using ZnO on Alumina

2,000 grams of the used Mack T7 oil from Example 1 was circulated at a rate of 2,000 ml/min through a filter containing 192 grams of ZnO on an alumina substrate. After 8 hours the viscosity of the oil was 22.3 centistokes at 100° C and 149.0 centistokes at 40° C. The amount of soot before and after contact with the ZnO on alumina was 20.5% and 9.4%, respectively, which corresponds to a 54.1% reduction in soot. The results obtained from this example are also summarized in Table 1 below.

Table 1

TGA Temp Region, ° C	Oil Fraction	% of Oil Fraction in Each Temperature Region Before and After Filtration			
		NaOH		ZnO	
		Before	After	Before	After
25-200	water + lt volatiles	1.3	1.4	1.1	0.8
200-400	oil basestock	77.8	85.8	76.1	87.8
400-600	pyrolyzable hydrocarbons	16.6	7.2	16.8	5.9
600-680	fixed carbon	4.0	3.5	3.7	3.5
Residue	ash	0.4	2.2	2.3	2.0
Total soot (400-680 ° C)		20.6	10.7	20.5	9.4
% reduction in soot		48.1		54.1	
Viscosity @ 100 ° C, cSt		26.6	17.7	26.6	22.3
@ 40 ° C, cSt		257.5	145.6	257.5	149.0

The data in Table 1 show that the untreated used oil (the Before columns) has an appreciable amount of soot (pyrolyzable hydrocarbons + fixed carbon) and that contact with a substrate containing a strong base significantly reduces the amount of soot in the oil (the After columns). The data in Table 1 also show that the reduction in soot corresponds to a significant reduction in viscosity.

### Claims

1. A method for removing soot from a lubricating oil used in a non-gasoline fueled internal combustion engine which comprises contacting the soot with a heterogenous strong base for a period of time sufficient to cause at least a portion of the soot to become immobilized on the strong base, wherein the strong base is barium oxide, calcium hydroxide, magnesium carbonate, magnesium hydroxide, magnesium oxide, sodium aluminate, sodium carbonate, sodium hydroxide or zinc oxide, or mixtures thereof.
2. The method of claim 1 wherein the lubricating oil containing the soot circulates within the lubrication system of an internal combustion engine, and the heterogenous strong base is immobilized within the lubrication system of the engine.
3. The method of claim 1 of 2 wherein the strong base is magnesium oxide, zinc oxide or sodium hydroxide, or mixtures thereof.
4. The method of claim 3 wherein the strong base is magnesium oxide or sodium hydroxide, or mixtures thereof.
5. The method of claim 4 wherein the strong base is magnesium oxide.
6. The method of any preceding claim wherein the heterogenous strong base is incorporated on a substrate.
7. The method of claim 6 wherein the substrate is alumina, activated clay, cellulose, cement binder, silica-alumina, a polymer matrix or activated carbon, or mixtures thereof.
8. The method of claim 7 wherein the substrate is activated carbon.
9. The method of any of claims 6 to 8 wherein the substrate is part of the oil filter system of the engine.
10. The method of any claims 2 to 9 wherein polynuclear aromatic compounds are also removed from the lubricating oil by contacting the oil with a sorbent located within the lubrication system.
11. The method of claim 10 wherein the sorbent comprises activated carbon.
12. The method of claim 10 or 11 wherein the sorbent and heterogenous strong base are included within the oil filter system of the engine.
13. The method of any of claims 10 to 12 wherein the heterogenous strong base is incorporated on a substrate and the sorbent and substrate comprise the same material.
14. The method of claim 13 wherein the sorbent and substrate comprise activated carbon.
15. The method of any of claims 10 to 14 wherein the sorbent is impregnated with at least one engine lubricating oil additive.

16. The method of claim 15 wherein the lubricating oil additive is an antiwear agent, an antioxidant or a friction modifier, or mixtures thereof.

17. The method of any preceding claim wherein the internal combustion engine is a diesel engine.

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